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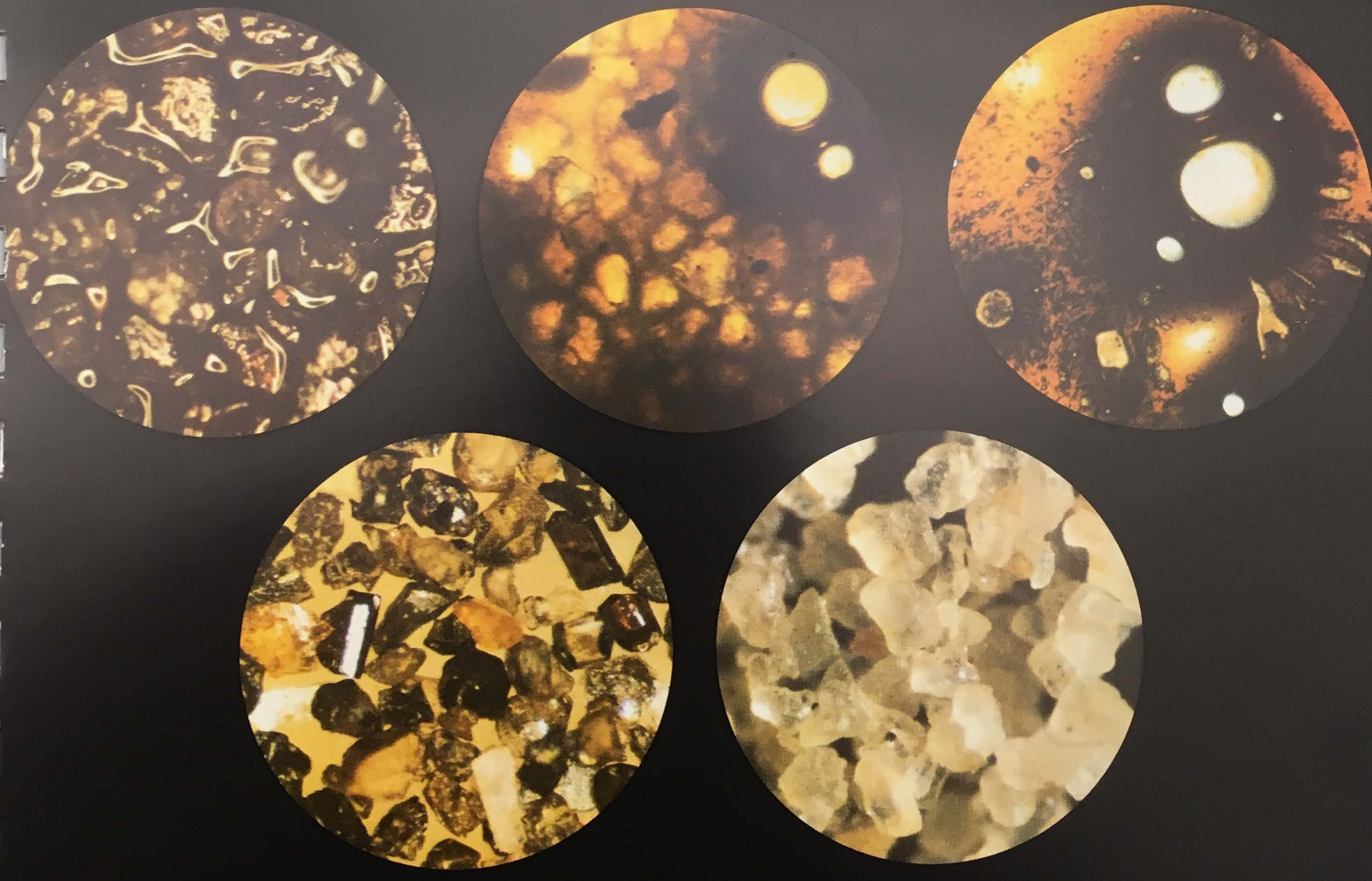

Oil/Water/Solids Analysis of Tar Sands -
A Review and Analytical Development

by

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ABSTRACT

A review is presented of past and present methods used to determine oil/water/solids, (O/W/S), in tar sand. It is concluded that the Dean-Stark method, currently used by Syncrude, and the industry, enjoys the most confidence at this time. Syncrude practise for sampling and sample preparation of tar sand is discussed along with an analysis of the basic, invariable parameters available for measurement. Problems with sample size are also considered. An ideal O/W/S method is identified and possible methods of achieving the ideal are examined. A simple, direct extraction technique of the type proposed, which is consistent with the identified fundamentals, appears to be most promising. For medium grade tar sand an error tolerance of ± 5% is possible for water determination and although stringent, ± 1.5% is a realistic goal for bitumen.

Keywords: Oil/water/solids analysis, Dean-Stark extraction C.P.A. Tar Sands Council, Sampling techniques, Sample size, Sample preparation, Errors, Tar Sand.

CONTENTS

1. SUMMARY

Over the past four decades, a variety of techniques have been at least examined, or used, to analyze tar sand. These include some methods developed in recent years which are at least in part instrumental in nature. However, the method that has been most extensively used in both the historical sense and in terms of current practise, and the one that enjoys the greatest level of confidence is essentially a separation method based on the Dean-Stark extraction technique. This method which was first developed in the early nineteen fifties, is now generally known as the Dean-Stark Method.

In developing a new O/W/S method it was considered critical to identify the variable and invariable parameters associated with tar sand analysis. The latter can give rise to precise and accurate results but the former are restricted to less precise, secondary or "quick and dirty" methods. Secondary methods have their value, but if a precise and accurate primary analytical method is to be considered then the measurement of mass in order to determine bitumen and solids in tar sand becomes a restriction. Because of the paramteres involved it is doubtful that a simple, precise, one step instrumental method will be developed in the near future.

Sample size was another important consideration in method development. It was concluded that on the basis of the current sample preparation technique a sample in the order of 50 to 100 g is required. The consequence of a large sample size is critical in that it restricts a choice of instrumentation for O/W/S work to that kind of equipment that is capable of accommodating large samples. If an improved procedure can be achieved then the sample size can be reduced and the corresponding restrictions imposed on instrument selection can be relaxed. This should open greater possibilities for overall O/W/S method improvement. Because of the advantages to be gained a major effort will be made towards sample preparation improvement.

Error associated with the O/W/S analysis was examined and considering the state of the art as indicated by the Canadian Petroleum Association study of 1973/74 in particular, an error tolerance of ± 5% would appear to be possible for water determinations in all but very low water samples. However, ± 1.5% in determining bitumen is a more stringent but still realistic limit for all but low bitumen samples as demonstrated by Syncrude and Hydrocarbon Consultants' results contained in that study. Until new error limits are identified by users of the analytical results, these limits will be used as criteria in developing a new O/W/S method.

As a result of the present study it was concluded that a direct extraction or elution technique is the most logical and promising direction for analytical development. A specific extraction technique is proposed which could be employed as an O/W/S method whereby the bitumen content is determined by difference. It is estimated that the total time for analysis might be about 45 minutes with this method as compared to the 8 to 18 hours required for the current method. Alternatively, the proposal might well serve as an important extraction step to be used in conjunction with a variety of instrumental methods. If this is possible then analysis time should be reduced to about twenty minutes. One operator should then be capable of approximately 70 O/W/S analyses per shift as compared to the 12 per shift with the current method. The savings to the commercial plant because of a faster O/W/S method should be something in the order of $200,000 annually, or about five million dollars over the lifetime of the plant.

2. CONCLUSIONS

1. Despite the time and cost requirements, the Dean-Stark extraction method continues as the most common and reliable method for O/W/S analysis.
2. Examination of the parameters by which bitumen and solids can be measured shows that mass is the only invariable parameter available. This parameter requires a separation technique.
3. The current sample size requirement of 50 to 100 g, which was born out of experience, is in agreement with a simplified theoretical study of the problem.
4. It is important to develop an improved sample preparation and homogenization technique in order to allow use of much smaller but still reliable sub-samples (i.e., 1 g or less versus 50 g). This will permit among other things exploration of a greater variety of possible instrumental techniques.
5. Development of a simple and accurate one step instrumental O/W/S method is expected to be slow because of the difficulty in identifying and utilizing parameters that can reliably measure the three tar sand components in the one step.
6. A simple, direct extraction or elution technique is proposed and is considered promising either as an O/W/S method in its own right or as an important extraction step to precede instrumental analysis.
7. Because of the different nature of froth and tailings samples it is quite likely that separate analytical methods will have to be developed for those substances.

3. RECOMMENDATIONS

1. Initiate an immediate program to develop an improved sample preparation and homogenization method.

2. Begin an immediate examination of the extraction technique proposal as outlined in Appendix C. Its use, particularly in conjunction with Liquid Chromatography and Nuclear Magnetic Resonance, should be fully examined.

3. Maintain current awareness with regard to possible instrumental O/W/S methods that have either primary or secondary analytical potential.

4. INTRODUCTION

The analytical method currently utilized by Syncrude and the industry in order to accurately assess tar sand reserves and monitor extraction processes is essentially a separation technique. As practised, particularly by Syncrude, the method yields highly reliable results. A serious disadvantage of the method, however, stems from the long analysis time of over eight and sometimes over eighteen hours, high operator requirements and consequently, high analysis costs. To carry out this one analysis for the commercial plant, the costs are expected to approach one quarter of a million dollars annually. In addition, the long analysis time will not allow the plant operators access to meaningful information regarding the quality of feedstock material.

A considerable need exists, therefore, to develop a new, fast and relatively simple O/W/S method for analyzing tar sand. Any new method must be as equally reliable as the current method.

5. HISTORICAL REVIEW

5.1 O/W/S Methods - A Resume of Past and Present Practises

The earliest known study concerned primarily with the analytical aspects of tar sand was that of Gilmore, Swinnerton and Connell (1), done in 1927. The primary O/W/S method utilized by these workers amounted to first air drying the sample because of *"the non-uniformity of the material in the samples submitted"*. The samples were exposed to the atmosphere in shallow pans in a warm room for, *"about 24 hours, although for very wet samples a longer time is necessary"*. The water content was then determined on an air dried sample according to a Dean-Stark method (ASTM D95-27). Finally, bitumen was completely extracted from a 500 to 1000 g sample in order to obtain the weight of the dried solids. The bitumen content was then obtained by difference.

An ashing method was also described by these workers whereby about 25 g of sample were ignited to constant weight in a muffle furnace. A *"loss of ignition correction"* was made in order to arrive at the final results. In this study the results of triplicate bitumen determinations by the ashing method were compared to a single result obtained by the extraction method. Although the results were in good agreement (i.e., 16.9, 16.8, and 16.7 versus 16.9% by extraction) the ashing method was considered desirable only to roughly check the extraction method or where only small samples were submitted.

W.J. Dyck in a 1944 study (2), proposed a density method as a rapid laboratory or field technique for determining bitumen in tar sand. In essence, the density and water content of a tar sand sample were carefully determined and from this data a calculation was made of the bitumen content.

The Fuels Division of the Federal Department of Mines and Technical Surveys then developed a carbon tetrachloride extraction method utilizing a standard Soxhlet apparatus and a paper thimble. The bitumen was extracted from a 50 g sample and from the weight of the remaining solids, the bitumen content was calculated on a dry basis. Water content was determined on another 50 g sample by distillation with naphtha (ASTM D95).

The Calvan Consolidated Oil and Gas Company during the early nineteen fifties (3) made an extremely important contribution in developing what is now commonly known as the Dean-Stark Method. Of all the methods developed before and since this is the one that has been the most extensively used, and the one that dominates current practise. It is basically a Dean-Stark extraction technique and in its original form required a 30 g sample. As a result of extraction with toluene the three components bitumen, water, and solids were simultaneously and physically separated and the latter two were measured by volume and mass respectively. Bitumen was then determined by difference.

In 1955, Draper, Yates, and Chantler (3) compared the density, carbon tetrachloride and Calvan or Dean-Stark methods. They concluded:

> *"Of the three analytical procedures, the toluene extraction method (Dean-Stark) gave the most uniform and accurate results. The precision of this procedure was slightly superior to the carbon tetrachloride extraction technique, and its accuracy was considerably better due to the more reliable moisture values obtainable by this procedure.*
>
> *The density method of bitumen assay was of a much lower order of precision than the two extraction procedures. Consequently, the density method should only be considered when it is not possible to use the extraction methods or when a high accuracy is not important."*

J.W. Milne, of Imperial Oil Ltd., in July, 1962 (4), and at the request of the Cities Service Athabasca Inc., Analytical Task Force, compared five different methods by determining the oil content of three standard samples of tar sand. This request had its origin in the "*difficulty ..... in finding methods which give consistent comparable results.*" The methods studied were:

1. Bailey-Walker, which was apparently a variation of and therefore a new name for the Dean-Stark method except that 100 g of sample was used rather than 30 g (Calvan) or 50 g (Draper et al).

2. Ultrasonic-Gravimetric Method, where 10 g of sample was extracted with 500 ml of benzene/acetone/methanol mixture and the residue was brought to consistent weight at 40°C.

3. Total Ash, where 1 to 2 g of sample was ignited to constant weight at 700°C.

4. Cities Service Spectroscopic Method, where 10 g of sample was agitated with 10 ml of water and 50 ml of benzene for 20 minutes. The absorbance of the benzene layer was then examined by Infrared Spectroscopy at 3.42 microns and compared against a calibration curve. This method had been described in a Mildred Lake Comparison of Analysis report of December 1961 (5), which stated: "*The oil content of the feed sand is obtained to a precision of about ± 3% by this procedure.*"

5. Multiple Extraction Spectroscopic Method, which was a variation of 4 except that the sample was extracted three times with smaller quantities of solvent.

Milne concluded that:

"Comparison of several available methods used in analyzing Athabasca Tar Sands has shown that all have their limitations. Certainly the most promising from the viewpoint of convenience, time needed for analysis and ability to turn out consistent results, is the CSAI spectroscopic method to which we have made our own modifications. This multiple-extraction method gives results which are about 5 to 7% higher than the best of the single extraction methods. These results also show better repeatability. Therefore, on a purely comparative basis this method must be recommended; however, it must be emphasized that our investigations have yielded no direct evidence that the method can measure absolute oil contents."

It is interesting to note that Milne was not particularly impressed by the Bailey-Walker (Dean-Stark) method. *"The results are reasonably reproducible but not consistent."* He also felt that water determined by a Dean-Stark trap was at best only approximate.

However, a September, 1962, study from the Richfield Oil Corp., Watson Laboratory (6), seriously questioned the use of the Infrared Spectroscopic approach.

"Scans were made of solutions of three different bitumens of identical concentrations. The scans for different bitumens are different and do not necessarily coincide at 3.42 microns .... We have found absorbancies at 3.42 microns are definitely not constant for the bitumens from different areas. Absorbancies will also vary according to the history of bitumens. From our work we find that the assumption that the absorbancies were identical for all bitumens at 3.42 microns was, unfortunately, without good foundation."

This same study also raised doubts about utilizing the visible region of the spectrum.

"Visible region scans were made of three solutions of different bitumens of identical concentrations. The curves of Areas A and B bitumens were close while Area 21 bitumen gave a prohibitively different scan. This information indicates that visible region absorbances cannot be used as a quantitative device for bitumens."

The consequence of these activities, apparently, was a reversion to a Dean-Stark method of analysis. The Syncrude Research Report of September, 1965 (7), stated:

"The analysis of tar sand and froth samples for oil, water, and solids is fundamental in the evaluation of the "Hot Water Process". In the past, these analyses have been inconsistent and many were in doubt. As an example, the analytical material balance for samples of tar sand from the 1962/1963 coring program averaged less than 98%, indicating that over 2% of the sample was not being accounted for. An analytical task force was set up in 1962 to review the entire analytical set-up at Mildred Lake. This group developed a new procedure, originally called the Richfield 3-in-1 Method, and now known as S.A.M. 2.1.1 (note 1965 numbering). This procedure resulted in a marked improvement in the analytical material balance for tar sand samples from the 1962/1963 coring program when retested in 1964, the analytical balance averaged close to 100%."

The name Richfield 3-in-l Method, appears to have been introduced as still another name for the Dean-Stark or Calvin Oil and Gas Method.

The procedure was "tightened" over the next two years (8,9), under the guidance of G.D. Hoggan of ARCO Chemical Company, in order to achieve the same level of analysis with froth and tailings samples as had been the case with tar sand samples. This effort tightened the analytical material balance for froth samples

from 99.97 ± 4.92 to 99.16 ± 1.92. The low average analytical material balance for froth samples was found to be mainly due to the bitumen determination. Although the froth samples were found to lose water on storage unless care was taken, the solids and water determination were found to be free of significant errors, thus making an oil content by difference approach feasible.

The Syncrude Research Report of 1967 (9), concluded that: "*Evaluation of several indirect physical methods (e.g., refractive index, infrared, etc.), to determine the bitumen content of the extract from tailings samples indicated that the infrared method provided the best instrument precision (2.5% error).*" A routine procedure developed by Syncrude was issued as S.A.M. 2.1.2. (Note 1967 numbering)

An attempt was later made to develop a rapid technique for O/W/S analysis utilizing a Varian PAT-20 N.M.R. instrument. Unfortunately, a variety of difficulties were encountered in trying to apply this instrument. As concluded in the Syncrude Research Department Annual Documentation of 1971 (10), "*Although capable of rapid determinations, the PAT-20 did not prove suitable for our requirements because of .... large analytical errors.*"

Although other methods were discussed, the Canadian Petroleum Association Tar Sands Council conducted a "round robin" study during 1973 (11), where, for the most part the Dean-Stark method was compared in its several, relatively minor variations amongst eight laboratories.

These laboratories were:

<u>Commercial Laboratories</u> -

Canada Core Analysts - Calgary

Core Laboratories - Canada Ltd. - Calgary

Core Laboratories - Canada Ltd. - Edmonton

Hydrocarb Consultants Ltd. - Ft. McMurray

<u>In-House Company Laboratories</u> -

Great Canadian Oil Sands Ltd. - Ft. McMurray
Imperial Oil Limited - Calgary
Shell Canada Limited - Calgary
Syncrude Canada Ltd. - Edmonton

Incidently, the Syncrude modification because of its careful attention to correction factors and its mass balance closure earned itself the special description, "Syncrude Method" in this study. This method, which is now known as S.A.M. 1.006, is presented in Appendix A.

Other methods that have been employed at one time or another are:

a) Retort: This method was described in the C.P.A. Study as follows:
"By this method the tar sand and water are virtually boiled off, condensed, measured, and empirically corrected for loss of light ends and coking. The empirical correction is derived through calibration by Dean-Stark. The advantages are speed and low cost. The disadvantage is the empirical correction which can introduce significant errors. We understand that some commercial laboratories will analyze with this method although they do not recommend it as a high confidence technique".

b) <u>Pressure Elution - Fischer Titration:</u> This method which is a direct separation technique, apparently had its origins with the Alberta Research Council. Further, it was the only non Dean-Stark method included in the C.P.A. Study and was described in that study as follows:
"To our knowledge Hydrocarbon Consultants is the only commercial laboratory that uses this technique and therefore we refer to it as Hydro-carb's. This method involves homogenizing a sample and splitting it into two parts. One part is put into a metal tube and bitumen is removed

through displacement by cold toluene. The tube and material are dried and the dry material weight determined. The second portion is treated with a tar-water solvent (methanol chlorothene mixture or tetrahydrofuran) and the dissolved water-tar mixture is analyzed for water content by Karl Fischer titration. Tar content is derived by difference between original weight and dry weight plus water. The advantage of this method is speed. The disadvantages are errors induced through dealing with two samples and errors inherent with the water measurement and therefore difference derivation for tar content".

c) Rapid and Convenient Laboratory Method for Extraction and Subsequent Spectrophotometric Determination of Bitumen Content of Bituminous Sands", by M.S. Patel, Alberta Research Council (12):

This method was described in the May, 1974, issue of Analytical Chemistry and appears to resemble the Pressure Elution method above. In brief, a 20 to 25 g sample is pressure eluted with toluene (10 to 20 psi) for a period of 10 to 20 minutes. The resulting extract is examined at 530 nm on a Spectronic 20 and the bitumen content is determined using a calibration curve.

The drawbacks to this last method are first, the apparent arbitrary choice of wave length and hence variability of that parameter in measuring bitumen. More serious is the fact that the method is incapable of determining water content, which must be done by the Dean-Stark method.

5.2 A Brief Note on the C.P.A. Round Robin Study

The C.P.A. study, although not exhaustive in terms of the number of determinations carried out and although possibly open to criticism in that laboratories were likely putting their best performance forward, has been none the less an extremely useful study especially for the purposes of this report.

The Abstract, Summary, Conclusions and Recommendations of the study are presented in their entirety in Appendix B.

6. DISCUSSION OF CONSIDERATIONS

If the development of a new and precise O/W/S tar sand analytical method is to proceed along sound rational lines it is imperative that the basic principles and limitations associated with the analysis be understood. Specifically, the parameters available for measurement, the sample sizes required, the consequences of sample preparation - particularly with regard to sample size, and finally, the error limits that are required or that are acceptable must be considered.

6.1 Quantitatively Characterizing Tar Sand

The object of the O/W/S analysis is to quantitatively describe, in terms of percentages based on mass, the composition of tar sand samples according to the three main components, oil (bitumen), water and solids. A fundamental requirement of accurate quantitative analysis is that a measureable parameter must be chosen that relates directly and invariably to the component being determined. The primary point of departure in developing an improved O/W/S method, therefore, is to clearly identify the fundamental, invariable and measureable parameters.

Of the three main components in tar sand, only water is a single, descrete, physical and chemical entity. Its presence in tar sand may be complex in terms of its chemical or physical relationships with the other components. Nevertheless, in theory, if not in practice, it is possible to remove the water and measure it by a variety of techniques, or measure it in situ. Only its loss in sampling, sample preparation and handling is of major concern.

Bitumen on the other hand, is an exceedingly complex and varying blend of a large number of organic molecules and small and varying amounts of elements such as Nitrogen, Sulphur, Nickel, and Vanadium. In addition, it has been defined from a working point of view, within Syncrude at least, as that organic material that is toluene extracted from tar sand. As a consequence of this definition the total organic content of tar sand is not a measure of bitumen content. It should be noted that ashing

or retort techniques were really attempts to measure total organic carbon in tar sand. These methods would therefore include coal etc. whenever present. In addition, to being at variance with the definition of bitumen these techniques are subject to interferences from inorganic carbonates.

Considering the problem of variability still further, the many variations that occur in the composition of extracted bitumen, including for example, the hydrogen to carbon ration (e.g. 1.39 to 1.50 in a given core hole (13)), and also the variations in U.V., Visible and I.R. absorption (6), all place serious restrictions on its quantitative characterization. In fact, there appears to be only one fundamental parameter that can reliably and quantitatively describe bitumen. That is mass, and it becomes obvious that to measure mass a separation step is required.

The final component, solids, also varies in composition and in fact varies widely from sand, to clays, to limestone. Elemental composition varies accordingly. The net result, therefore, is that there is only one fundamental parameter that can quantitatively characterize solids and that also is mass. If this parameter is to be utilized a separation technique is again dictated.

It should be emphasized that utilizing parameters other than mass is entirely possible as long as the variability in the chosen parameter is within the acceptable error limit. Or, conversely, as long as the users of the analytical data are willing to accept the errors associated with the variability in the parameter. Variable parameters can, and do, find analytical application in secondary or "rough" methods where precision is not of prime importance. In fact, specific suggestions will be made for secondary, O/W/S tar sand methods. However, if results are required having a high level of precision and accuracy, (i.e., comparable to the current Syncrude method) then development of a fast, reliable, separation technique appears inescapable.

6.2 Sample Size and Sampling Error

Any analytical method that requires the use of a minute, representative sample taken from a large quantity of parent bulk material must necessarily reckon with the size of the sample that will permit sampling errors to remain within acceptable limits. This is in contrast to on-line methods that are able to view all, or large fractions of the bulk material during analysis. Sample size and the associated sampling error (not to be confused with analysis errors) are therefore among the fundamental points for consideration in the development of a reliable analytical method for they can dictate the choice of instrumentation.

Establishing the correct sample size is not a straight forward matter. Experience within Syncrude suggests a tar sand sample size for O/W/S should be in the region of 50 to 100 g. Draper, Yates and Chantler *(3)*, utilized 50 g samples although they referred to the Calvan Oil and Gas Company recommendation of 30 g.

An independent approach to sample error and hence sample size determination has been possible through the recent work of Harris and Kratochivil *(14)*. The study identifies the number of particles or "units" of material that must be included in a model sample (which is simple in terms of sizes and type of components) in order to remain within an identified sampling error. Once the sample particle size can be established a calculation of sample volume and hence, sample weight is then possible. The larger the particle, the larger the sample. By making a few simplifying assumptions and approximations the findings of the Harris and Kratochvil study *(14)* can be applied to the problem of O/W/S analysis.

However, a consideration of particle size and in fact the nature of the tar sand particles must take into account the problems of heterogeniety that arise in obtaining O/W/S samples from drill core. Bands of lean, medium and rich tar sand varying in width from inches to feet can be abruptly separated by bands of varying width of clay, limestone, sand etc. This stratification is recognized in the correct sampling process by taking material from the core, for a given sample, from a

length of relatively homogeneous material. That is, the separation of large bands of a given substance are respected and a sample is confined, for the most part, to a given band. Problems of gross heterogeneity are therefore circumvented. Nevertheless, small intrusions of one mineral substance into the bands of tar sand often occur and it is this type of heterogeneity, as well as the heterogeneity occuring within a tar sand band, that must be considered in describing particle size.

If tar sand were a relatively homogeneous material it would be a reasonable approximation to consider particle size as being due entirely to the size of the sand grains, clay particles, etc., that make up the solid phase. These particles will be arbitrarily defined here as "native particles".

However, because the effect of distinct bands of material A intruding into material B must be considered it is reasonable to assume that during the sample preparation step the particles that result from the chopping and blending action remain discretely A and B, although distributed randomly. These particles are defined here as sample particles and such sample particles will contain native particles as suggested in Figure 1:

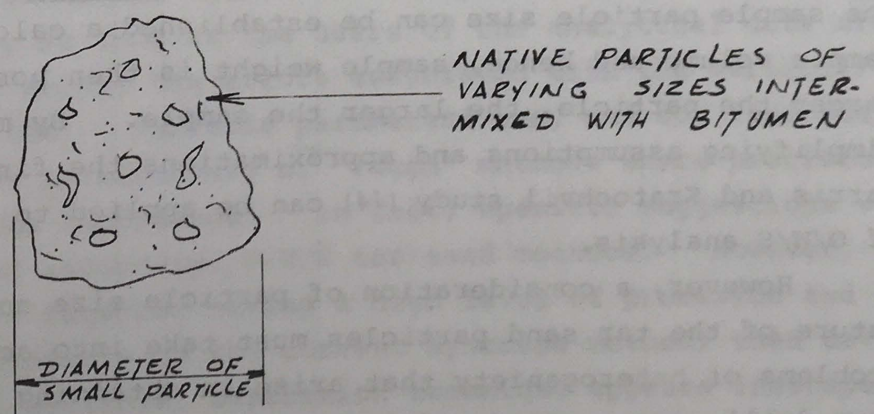

FIGURE 1.

It should be noted that it is the size of these sample particles not the native particles that must be considered in establishing sample size.

Current Syncrude practice is to prepare samples for O/W/S by chopping to 1/16 inch (i.e., 4 mm^3) sample particles. To establish the effect of particle and hence sample size by applying the Harris and Krachtovil study (14), consider the two possible extreme cases that occur in sampling. In the first case a tar sand sample, rich in bitumen (i.e., 16% bitumen), can also contain quantities of clay, sand or limestone containing zero bitumen. Assuming each of the two kinds of particles are reduced to 1/16 inch and that a sampling error of 1% (relative standard deviation) is acceptable, then the sample must contain about 2×10^3 particles. This is equivalent to about 21 g of tar sand (i.e., 8 cm^3). Note that if the sample preparation is able to reduce particles to only 1/8 inch instead of 1/16 inch, then for the same number of particles required, the sample weight increases by a factor of 8 to about 160 g. Also according to the study, lower grade tar sands also reduced to 1/16 inch particle size, require a greater number of particles - and hence sample size - to maintain a sampling error no greater than 1%. For example, 10% bitumen tar sand would require slightly more than 100 g and 6% tar sand would require about 200 g as compared to the 21 g required of 16% tar sand.

The second case, and the other extreme, would be one where a sample was obtained entirely from a reasonably uniform band of rich tar sand having no intrusions of foreign material. If it is assumed that the bitumen varies between 13% and 16% in discrete, uniformly sized particles of prepared sample then less than 100 particles are required in a sample in order not to exceed a 1% sampling error. This is equivalent to a sample weight of less than 1 g.

As the degree of uniformity or homogeneity improves in the extreme and if it assumed that bitumen is uniformly coated over the native particles, then eventually it is the number of native particles, not sample particles, that establish sample size. This would be the case with an ideal sample preparation method using a sample taken from a uniform bed of tar sand.

Finally, if the sampling error is to be reduced by a factor of 10 to 0.1% then the sample size described above would have to increase one hundred fold. That is, a lean tar sand sample (i.e., 6% bitumen) containing foreign material (case one) would require a 20,000 g sample. Even a rich, uniform tar sand described above in case two, would require a sample in the order of 100 g instead of 1 g. Acceptance of a realistic sampling error, suggested here as 1%, is therefore inescapable regardless of the analytical method employed.

Considering the wide variety of tar sand samples that must be dealt with routinely by any O/W/S method, case one probably represents the most realistic basis for determining sample size. The possible range of from 21 to about 200 g of sample cited above is consistent with the industry experience with size requirements, which have been shown to range from 25 to 100 g. Any new routine O/W/S method, therefore, must be capable of processing a sample of no less than 50 grams, based on the current sample preparation procedure. The sampling error associated with this weight will increase above 1% as heterogeniety of the material increases and decrease as heterogeniety decreases. As an approximation, the effect of the sampling error on the values reported for oil, water and solids will normally be less than 1% of the stated value as compared to the bulk material from which the sample was taken.

6.3 Sample Preparation Problems

Because it is necessary to consider sample particle size and homogeniety in relation to sample size, it in turn becomes necessary to consider the sample preparation method necessary to achieve the desired sample reduction.

The current procedure for preparing a sample is tedious, time consuming, and hence, costly. It is used reluctantly by Syncrude and the industry because a better method for reducing and homogenizing such a difficult and tacky material-without loss of volatile components - has yet to be devised. The current method requires repeated, manual chopping, quartering, and coning until 1/16 inch size is obtained. In addition to

the deficiencies of time and tediousness, the method probably gives rise to considerable water loss because of the necessary and prolonged exposure of the sample to the atmosphere. The degree of error associated with this loss is not known. However, the experience and concern over water loss during the C.P.A. Tar Sands Council Round Robin Study (11), would suggest that it could be appreciable. It is entirely possible that the current sample preparation procedure could be a major source of error in O/W/S analysis.

The development of an improved procedure will likely be difficult because of the fouling and cleaning problems of apparatus and because of the restrictions of no volatile losses. Nevertheless, it must be done in order to give a faster, more homogeneous sample composed of particles approaching the size of the native particles as discussed in the previous section.

R.E. Hoyle and C.G. Paton have carried out informal studies using low temperature samples (about -23°C, -10°F) and a hammermill. These experiments showed reduced fouling and the approach therefore has promise. C.G. Paton has suggested sample temperatures should possibly be in the order of dry ice (-78°C). In addition, it may also be necessary to add liquid nitrogen (-196°C) dropwise into the hammer mill to ensure non volatility and solid, non adhesive behaviour of the samples during reduction. This type of procedure, incidentally, is apparently used in preparing teflon samples for analysis. The safety aspects of working with liquid nitrogen, and with the hammer mill, at extremely low temperatures must be given every consideration.

The consequence of a large sample size is critical in that it restricts a choice of instrumentation for O/W/S work to that kind of equipment that is capable of accomodating large samples. If an improved procedure can be achieved then the sample size discussed previously can be reduced and the corresponding restrictions imposed on instrument selection can be relaxed. This should open greater possibilities for overall O/W/S method improvement. Because of the advantages to be gained a major effort will be made towards sample preparation improvement.

6.4 Error in O/W/S Analysis

The final factor that must be considered in designing a new analytical method is the degree of error allowable in the analysis. The C.P.A. study considered the error of an O/W/S analysis as follows (11, p.3).

> "*A term of reference critical in our examination was degree of accuracy of the assay analysis acceptable to a company. As previously discussed, we recognize that this will vary from company to company but it was generally concluded that an analysis value for an average grade tar sand was acceptable if it fell within the true value by ±5% with a high degree of confidence (90-95%), i.e., if a true value was 12.0% bulk weight, values between 11.4% and 12.6% would be acceptable. This tolerance should probably be higher for lower bitumen saturations, i.e., 4% - 5% bulk weight.*"

In the above study, the "true value" was taken to be the overall average of assay results. Strictly speaking the study is therefore addressing itself to the matter of precision. That is, it was concerned with reproducibility (the variations that occur in repeating the same analysis amongst several laboratories) and repeatability (the variability that occurs when repeating the same analysis by the same method, apparatus, etc., within a given laboratory). However, the difficulties inherent in obtaining a true value in the deposit from which a sample came (i.e., a matter of accuracy) are well recognized. The degree of deviation or lack of it from the overall average, which has been considered to be the "true value", is therefore a good <u>indication</u> of accuracy.

A summary of the data of the C.P.A. study is presented in Table I (% Bitumen Based on Bulk Weight) and Table II (% Water Based on Bulk Weight). The results of only three of the eight laboratories are included in these tables. The laboratories in question are Syncrude (modified Dean-Stark method), Hydrocarbon Consultants (direct extraction and bitumen by difference method) and for comparison, G.C.O.S. (Dean-Stark method).

TABLE I

% of Bitumen Based on Bulk Weight
(Taken from Data from C.P.A. Tar Sands Council Round Robin Study 1973/74)

LABORATORY		CATEGORY								
		LEAN			MEDIUM			RICH		
	No. of Det'ms	Mean	Std. Dev.	% Dev.	Mean	Std. Dev.	% Dev.	Mean	Std. Dev.	% Dev.
All Labs	80	10.01	0.30	-	11.49	0.28	-	14.37	0.20	-
		(95% Conf. level = 0.59 or 5.9% of mean)			(95% Conf. levels = 0.55 or 4.8% of mean)			(95% Conf. level = 0.39 or 2.7% of mean)		
Syncrude	10	10.09	0.17	+0.8%	11.65	0.14	+1.4%	14.44	0.12	+0.5%
Hydrocarbon	10	10.08	0.32	+0.7%	11.58	0.32	+0.8%	14.19	0.40	-1.3%
G.C.O.S.	10	10.33	0.22	+3.2%	11.77	0.17	+2.4%	14.32	0.10	-0.3%
		(Max. Dev. of all labs) = +3.3%			(Max. Dev. of all labs) = +2.4%			(Max. Dev. of all labs) = -1/3%		

TABLE II

% Water Based on Bulk Weight
(Taken from Data from C.P.A. Tar Sands Council Round Robin Study 1973/74)

LABORATORY	No. of Det'ms	LEAN Mean	LEAN Std. Dev.	LEAN % Dev.	MEDIUM Mean	MEDIUM Std. Dev.	MEDIUM % Dev.	RICH Mean	RICH Std. Dev.	RICH % Dev.
All Labs	80	3.38	0.49	-	2.31	0.88	-	0.42	0.26	-
		(95% Con. level = 0.97 or 29% of mean)			(95% Conf. level = 1.71 or 74% of mean)			(95% Conf. level = 0.51 or 121% of mean)		
Syncrude	10	3.70	0.24	+ 9.5%	2.17	0.87	- 6.1%	0.36	0.21	-14%
Hydrocarbon	10	3.26	0.57	- 3.5%	2.36	0.63	+ 2.2%	0.58	0.44	+38%
G.C.O.S.	10	2.63	0.30	-22%	1.49	0.68	-36%	0.22	0.18	-48%
		(Max. Dev. of all labs) =-22%			(Max. Dev. of all labs) = -36%			(Max. Dev. of all labs) = -48%		

The % Deviation columns of Table I show that insofar as the bitumen determination is concerned the ±5% error tolerance was met with relative ease particularly by both Syncrude and Hydrocarbon Consultants. Syncrude showed the greatest deviation with a value of +1.4% for the medium grade tar sand. Hydrocarbon Consultants was very close with a maximum deviation of -1.3% for the rich tar sand.

The error tolerance criteria can also be considered on the basis of whether or not the 95% confidence limits were exceeded. The C.P.A. Study, incidentally, was primarily concerned with this approval. The 95% Confidence level presented in Tables I and II "indicates the limits beyond the mean within which a single analyzed sample should fall for each laboratory or within a laboratory's results should fall for each category with 95% confidence" (11, p.11). If this statistic is utilized in considering error tolerance, then the tolerance derived from all laboratory results is exceeded slightly in the lean category (i.e., 0.59/10.01 x 100% = 5.9%), but met in the medium category (0.55/11.49 x 100% = 4.8%) and also in the rich category (0.39/ 14.37 x 100% = 2.7%). The 95% confidence level value, incidently, is equal to 1.960 times the standard deviation arrived at for all laboratory results.

Insofar as the determination of water is concerned, the error tolerance as a rule is exceeded as gauged by either the % deviation of the individual laboratories or 95% confidence levels (all eight laboratories) in Table II. The exception, interestingly enough, occurs with Hydrocarbon Consultants where the limit was met by the % Deviation in two out of the three categories.

Water loss in sampling, sample preparation and transfer was identified in the C.P.A. study program as a basic problem. In fact it was stated (*11, p.19*):

> *"The wide deviation of results is evident not only from laboratory to laboratory but also within the individual laboratory. This probably reflects the difficulty in capturing and measuring the water as pointed out in the*

critique of laboratory procedures. Here it was pointed out that water measurement was probably the major source of error in the entire test procedure. The data probably also reflects the difficulty in homogenizing samples high in water content or a combination of these two reasons."

Summarizing the subject of error in O/W/S analysis and considering the state of the art as indicated by the C.P.A. study, particularly, an error tolerance of ±5% would appear to be possible for water determinations in all but very low water samples. However, ±1.5% in determining bitumen is a more stringent but still realistic limit for all but low bitumen samples as demonstrated by Syncrude and Hydrocarbon Consultants' results. Until new error limits are identified by users of the analytical results, these limits will be used as criteria in developing a new O/W/S method.

7. A GENERAL COMPARISON OF SYNCRUDE AND HYDROCARBON CONSULTANTS O/W/S RESULTS

Given the analysis of parameters in section 6.1, and the consequence of having to measure the mass of some components by a fast separation technique, it is extremely useful to compare Syncrude results (modified Dean Stark method) and the Hydrocarbon Consultants results (pressure elution or direct extraction). This comparison has of course been done through the C.P.A. Round Robin Study and only requires a re-examination of Tables I and II in the preceeding section.

The C.P.A. concern about the deficiences of the Hydrocarbon method not withstanding, the results on the basis of accuracy as measured by the % Deviation data of Tables I and II, force the conclusion that the method is at least as good as the Syncrude method. However, the precision of the Hydrocarbon method as shown by that laboratory's greater standard deviation in Tables I and II is not as good as that of Syncrude's. In fact, the C.P.A. Study commended Syncrude for its consistency in results which ultimately arises from a responsible and meticulous approach to analysis. But the C.P.A. study concluded (Appendix B), *"Consistency of results indicate that no one laboratory or technique showed superiority over another within the accuracy demanded for the tar grades examined. Hydrocarb and Shell laboratory data compared favourably with other laboratories with respect to the mean but exhibited wider variation between samples and hence wider 95% confidence levels than the overall category for the bulk weight and tar weight categories."*

As a consequence of this comparison, a direct extraction technique where possibly one component is determined by difference has been shown in practice to be a completely valid approach to o/w/s analysis. Considering the speed (and therefore economy) claimed for the Hydrocarbon method, and for the similar method of Patel (12), an elution or extraction method is a logical direction for development.

8. THE IDEAL TAR SAND O/W/S METHOD: IDENTIFIED CRITERIA

The following, which for the most part arise out of the preceeding discussion, are the criteria that would form the basis for developing an "ideal" method for tar sand analysis.

<u>Reliability</u>

1. Utilizes a single sample for all determinations.

   Reason: Avoids errors and discrepancies between different samples.

2. Able to utilize large samples (30 g to 100 g).

   Reason: Large samples required to avoid serious sub-sampling problems resulting from the <u>current</u> preparation method.

3. Each of the three major components is specifically determined to a level of precision and accuracy equivalent to that of the current method. Water to ± 5% of value and Bitumen to ± 1.5% of value reported (for medium grade tar sand).

   Reason: A material balance closure occurs with each analysis (i.e., totaling to 100%). This gives rise to maximum confidence in results.

<u>Costs</u>

4. Requires simple equipment.

   Reason: Minimizes maintenance costs and down time.

5. Requires a minimum number of operations.

   Reason: Minimizes technique and calculation errors as well as minimizing operator time and hence analysis costs.

6. Should utilize inexpensive and readily obtainable reagents and material.

   Reason: Minimize analysis costs and the risk of down time due to supplies being unavailable.

<u>Safety and General</u>

7. Should utilize non-hazardous reagents and equipment.

   Reasons: Personnel safety.

8. Can be performed by relatively untrained personnel.

   Reasons: Anticipated difficulty in obtaining personnel in Fort McMurray.

9. Total turnaround time should preferably be in minutes and at least within the order of about one hour.

   Reasons: Allows for effective plant control.

9. POSSIBILITIES FOR DEVELOPMENT

A. An Extraction/Elution Approach:

It has been pointed out in section 7, that development of a fast and reliable direct extraction (i.e., separation) technique appears to be the most logical direction for developing a new tar sand O/W/S method. This is not to say that one-step instrumental methods should not be investigated, especially if the problems of sample size reduction and homogenization can be overcome. In fact, suggestions for possible and simultaneous instrumental approaches will be made. However, prospects are not bright at this time for developing in the near future, a simple and reliable one step instrumental technique. If nothing else, therefore, a new method is required as an interim measure during instrumental development. In addition, an improved bench method will be required in the long term as a back up and check method to any instrumental technique.

An improved O/W/S method is possible, as long as the deficiencies such as those in the Hydrocarbon method can be overcome without loss of the advantage of speed. The main criticism of the Hydrocarbon method in the C.P.A. study was the necessity of dealing with a second sample in order to measure water content. The errors arising between samples then reflects itself in the bitumen result, which is obtained by difference. Any new direct extraction (separation) method must therefore be capable of utilizing one sample, be capable of measuring water, and preferably operate at very low pressures and meet or nearly meet the criteria of the Ideal Tar Sand O/W/S method.

The problem of determining water in a single tar sand by an extraction technique can be overcome if a solvent system can be developed that is capable of extracting both the bitumen and the water. It is extremely important to recognize that once a quantitative separation has been made between the solids, and the water and bitumen then a wide variety of options become available since the number of parameters by which bitumen can be measured increases. For example, the water in the extract could be determined by automated Karl Fischer and the bitumen

in the sample by difference, or, the bitumen could be determined directly by evaporation of an aliquot of extract, which could be carried out on possibly every tenth sample, but on a random basis, in order to provide material balance closures.

Alternatively, instrumental techniques might be applied effectively. For example, water and bitumen could be possibly determined in the extract using Liquid Chromatography and the soon to be marketed flame ionization detector. With the solids now removed N.M.R. could possibly make the same determination as long as a suitable non-interfering solvent could be employed. In either case, the solids, which are of least interest, could then be done by difference. If this is possible then a major saving in time should be achieved since a long drying period is normally required before the solids can be weighed.

Preliminary laboratory studies have shown that it is in fact feasible to develop a solvent system capable of extracting both bitumen and water. Varying blends of toluene and I.P.A. were used to dissolve measured quantities of bitumen and distilled water. The bitumen and water were present in each instance on a 2:1 mass ratio basis. Basically, 20 ml of solvent blend were used to dissolve 1 g of bitumen and 0.5 g of water. The results are descriptive and only semi-quantitative and are presented in Figure 2.

Figure 2

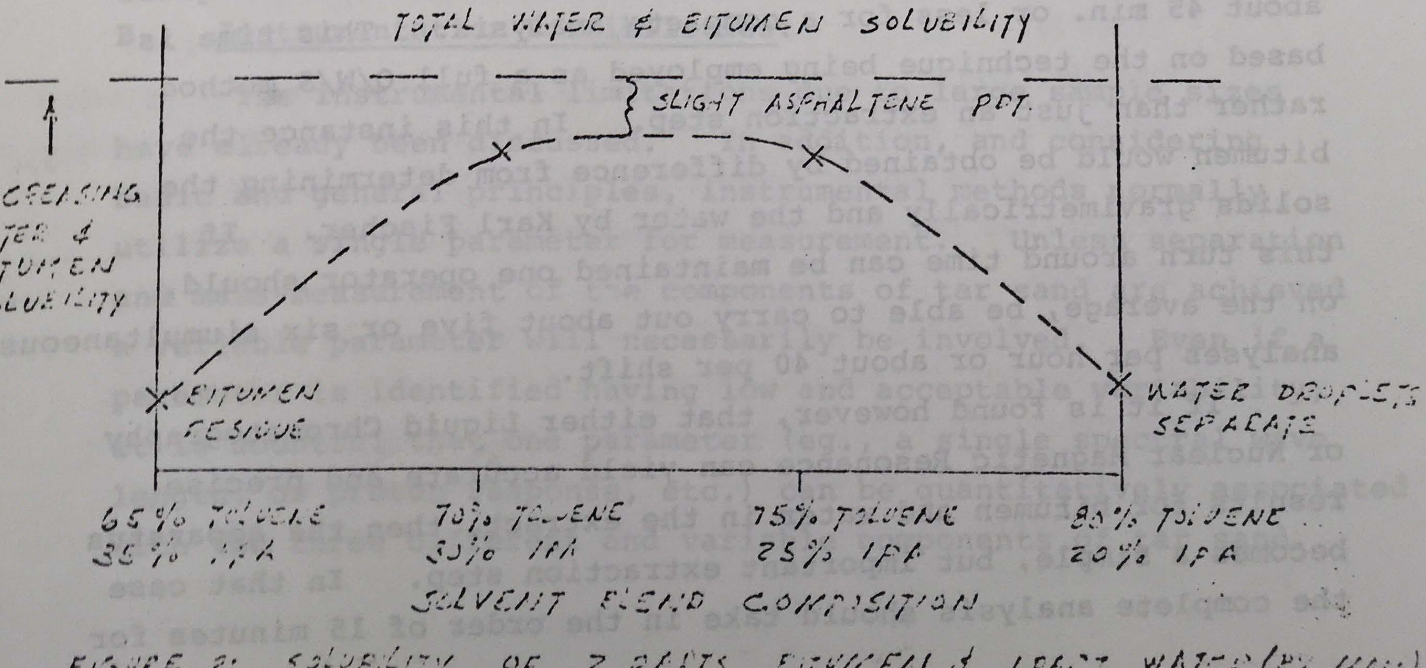

FIGURE 2: SOLUBILITY OF 2 PARTS BITUMEN & 1 PART WATER (BY MASS) IN 20 PARTS SOLVENT BLEND (BY VOLUME)

A solvent blend between 70%/30% and 75%/25% Toluene to I.P.A. appeared to be nearly ideal in order to dissolve bitumen and water. As shown in Figure 2, 20 ml of solvent was almost capable of holding in solution 1 g of bitumen and 0.5 g of water. A small quantity of asphaltenes quickly precipitated out of solution. Not surprisingly though, 30 ml of solvent was able to dissolve the stated amounts, but 10 ml of solvent left large amounts of residue that, interestingly, were subsequently found to be insoluble in pure toluene.

A water/bitumen solvent system must of course be studied in more detail and in a quantitative fashion. In addition, other solvents such as 1 methyl - 2-pyrrolidone suggested by J. E. Filby should also be examined. Nevertheless, the preliminary study showed that a bitumen/water solvent is a distinct possibility. In terms of an O/W/S method approximately 200 to 250 ml of such a solvent would be required to elute the bitumen and water from 50 g of very rich tar sand (i.e., 18% bitumen).

A simple extraction apparatus is proposed in Appendix C. This proposal utilizes the sonification effect to enhance the extraction as it was found in the preliminary studies to be extremely effective in putting bitumen from tar sand into solution. In addition, lumps of clay readily disintegrated so that channeling problems are not expected.

On the basis of extraction times quoted by Patel (12) and that by Milne (4), the proposed scheme is estimated to require about 45 min. or less for a complete analysis. This time is based on the technique being employed as a full O/W/S method rather than just an extraction step. In this instance the bitumen would be obtained by difference from determining the solids gravimetrically and the water by Karl Fischer. If this turn around time can be maintained one operator should, on the average, be able to carry out about five or six siumultaneous analyses per hour or about 40 per shift.

If it is found however, that either Liquid Chromatography or Nuclear Magnetic Resonance can yield accurate and precise results for bitumen and water in the extract, then the apparatus becomes a simple, but important extraction step. In that case the complete analysis should take in the order of 15 minutes for

extraction and 5 minutes for instrumental analysis for a total turn around time of about 20 minutes. Since the solids would be determined by difference, important savings in time would be realized. Under these circumstances one operator should be able to carry out about 10 analysis per hour or in the order of about 70 per shift.

Considering the savings that are potentially involved and that the output per operator using the current O/W/S method is about 14 analyses per shift, it is entirely realistic to see the Commercial Laboratory O/W/S analyses costs drop from a projected $250,000 to $50,000 per year, or less. Over the 25 year lifetime of the plant, these savings should total in the order of $5,000,000.

Finally, it is important to realize that the proposed extraction method of Appendix C is a means to establish the principles involved and a means of opening up a great variety of additional options. For example, continuous centrifugation and a "paint shaker" approach have been suggested and it is likely that many such options will become apparent as work proceeds. It is also important to realize that the proposed method will likely not be employed in analyzing froth and tailings samples as is the case with the current method. Because of the distinct and different nature of these latter samples distinct and more appropriate analytical methods will have to be developed.

B. <u>Instrumentation Possibilities</u>:

The instrumental limitations due to large sample sizes have already been discussed. In addition, and considering basic and general principles, instrumental methods normally utilize a single parameter for measurement. Unless separation and mass-measurement of the components of tar sand are achieved a variable parameter will necessarily be involved. Even if a parameter is identified having low and acceptable variability, it is doubtful that one parameter (eg., a single spectral wave length, or proton response, etc.) can be quantitatively associated with the three different and variable components of tar sand.

Because of this, development of an accurate and precise one step instrumental O/W/S method is expected to be slow and difficult.

However, utilizing instruments for secondary, less precise O/W/S analysis, and employing a variety of instruments in conjunction with the proposed extraction method, as already discussed, are both highly likely. Some of the instrumental techniques that have been considered are:

(i) X-Ray Fluoresence - this instrument may have good secondary method possibilities at least, and could depend upon the variability in concentration of elements such as Nickel and Vanadium in bitumen.

(ii) Infrared - a new reflectance infrared analyzer has been considered and because recent studies in the near IR region show good O/W/S potential, this technique is promising. It is doubtful, however, that the precision and accuracy by this technique would approach that of the Dean-Stark method because of the work of Hoggan (6). Even if it is not found suitable as a primary technique, it may prove to be suitable for on-line use, possibly as a trend analyzer.

(iii) Pulsed N.M.R. - this technique has been suggested by the Alberta Research Council in particular as a possible one-step technique. Uncertainties exist about the problem of sample introduction as well as about the proton response of solids bound water versus the proton response of the liquids. Of the two instrument suppliers, the Praxis Corporation has expressed enthusiasm but has not responded to specific questions about the application. The technique will be kept under investigation at least until Bruker Scientific has reached a conclusion regarding tar sand analysis.

As already suggested, N.M.R. could well find O/W/S application in conjunction with the proposed extraction method. This application will require a careful choice of an extraction solvent in order that the presence of the solvent in the extract can be easily and quantitatively identified.

(iv) Proton Activation - the Texas Nuclear Corporation recently proposed measuring bitumen and water via a proton activation approach and measuring water content by a micro wave method. It was pointed out that not only does the H/C ratio vary, which would give erroneous bitumen results, but bitumen has been found to strongly interfere with micro waves. This approach is not considered promising.

(v) Pyrolysis/Gas Chromatography - this technique is under active development in the U.S. for use in kerogen analysis of oil shales. The marked differences between tar sands and oil shales will not permit a simple transfer of experience, but this technique should be kept under active investigation as a possible primary method. The Chromalytics Corporation markets a thermal chromatography instrument capable of generating both a thermogram and a chromatogram and would appear well suited to our needs. However, an improved sample reduction method becomes critical for this technique because of the very small sample size involved.

(vi) Liquid Chromatography - as already suggested, this technique may find ready application in determining bitumen and water in the extract. The success of the application will depend to a large extent on the success of the new flame ionization detector to be marketed by Trocor, Inc., and by the satisfactory choice of extracting solvents.

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APPENDIX A

S.A.M. 1.006 - The Current Syncrude Tar Sand O/W/S Method

Determination of Bitumen, Water, and Solids Content of Tar Sand and Reject Samples

Scope: This method is intended for the determination of bitumen, water, and solids content of tar sand and reject samples, initially prepared as per S.A.M. 1.001 and S.A.M. 1.002 respectively.

Summary: The sample is separated into bitumen, water, and solids by refluxing with toluene in a solids extraction apparatus. Condensed solvent and co-distilled water are continuously separated in a trap, the water being retained in the graduated section. The solvent recycles through the extraction thimble to further dissolve the bitumen. The bitumen/solvent and nonfilterable solids fractions are subsequently separated by centrifuging. An aliquot of the resultant bitumen extract is evaporated to remove the solvent. The weight of bitumen is determined, gravimetrically after applying corrections for residual toluene content.

Safety Considerations:

1. Toluene - Mildly toxic by skin absorption and inhalation. Extremely flammable.

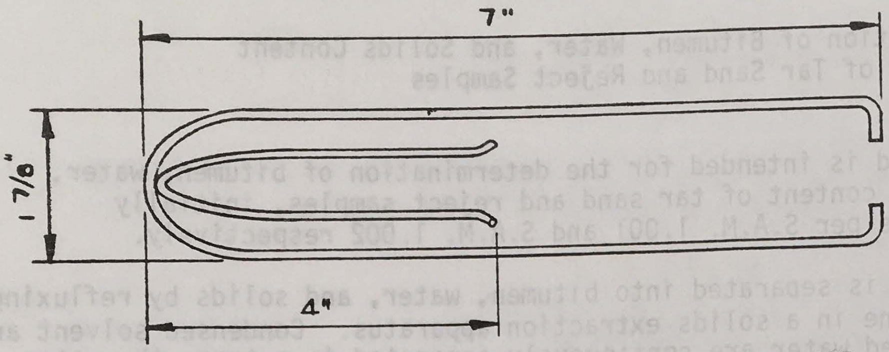
2. Isopropyl Alcohol - Irritant to skin and respiratory tract. Flammable.

3. Trichloroethylene - Very toxic by inhalation. Ensure adequate ventilation (fume hood).

Apparatus, Reagents, Materials:

1. Condenser - A straight tube condenser having a water jacket at least 400 mm long. West type condenser with 24/40 standard taper joint as specified in ASTM E 123 most suitable.

2. Water Trap - The trap shall be of 10 ml capacity having 24/40 standard taper joints. Design similar to that described in ASTM E 123. Traps shall be graduated at 0.1 ml intervals with a maximum scale error of 0.1 ml.



NOTE: FABRICATE FROM 14 GA. NICHROME OR CHROMEL WIRE.
SILVER SOLDER BOTTOM JOINT.

FIGURE 1. THIMBLE BASKET SUPPORT

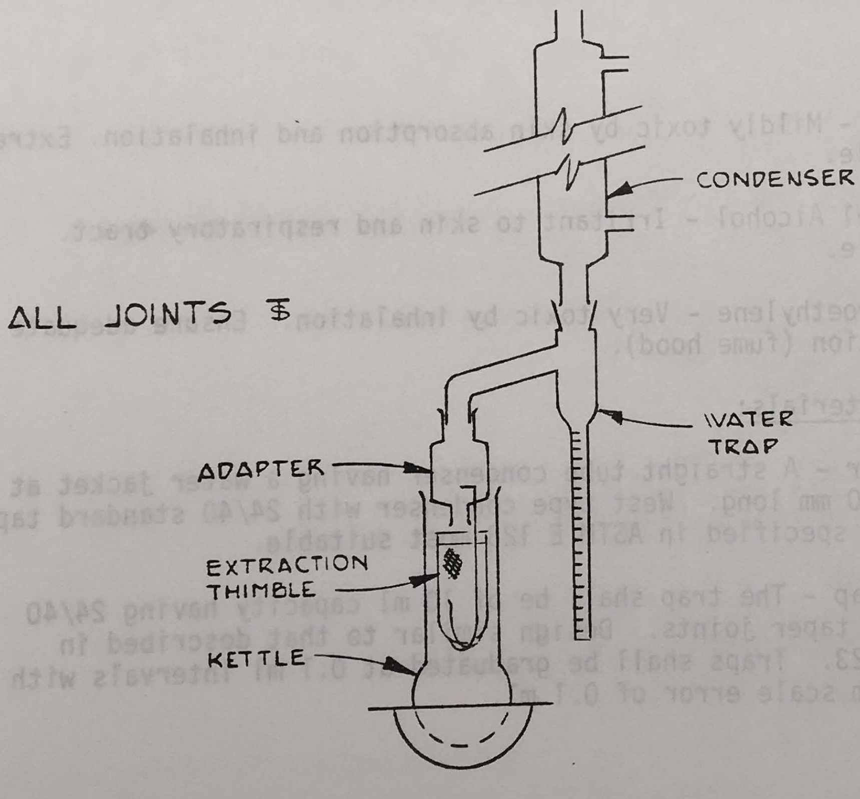


FIGURE 2. EXTRACTION APPARATUS ASSEMBLY

3. Kettle - A heat resistant glass vessel having a nominal capacity of 500 ml. The neck shall be a minimum of 250 mm long, including a 55/50 standard taper female joint to accomodate adapter.

4. Kettle-to-trap Adapter - This has a 55/50 standard taper male joint with a perforated downcomer extending below the ground glass surface. The upper part of the adapter is fitted with a 24/40 standard taper female joint.

5. Extraction Thimble - Whatman 43 x 123 mm paper thimble, single fat extracted.

6. Thimble Basket - A corrosion resistant basket to support thimble. See Figure 1.

7. Solvent Distributor - A corrosion resistant screen to snugly fit over open end of thimble.

8. Heating Mantle - 250 watt, Glas-col, to fit 500 ml kettle.

The assembled extraction apparatus is shown schematically in Figure 2.

9. Kimwipes - type 900-S

10. Weighing Bottles - Short form, 50 x 140 mm of borosilicate glass, with a 55/12 ground glass rim.

11. Centrifuge - IEC International Centrifuge Size 2 (floor model with timer) or equivalent, complete with Fisher Cat. No. 5-155 eight place head.

12. Centrifuge Tubes - 100 ml conical, graduated

13. Supply of 250 ml volumetric flasks, conforming to NBS specifications.

14. Recording IR Spectrophotometer, Beckman Acculab 4 or equivalent.

15. Matched pair NaCl cells, spectral path of 0.5 mm.

16. Evaporating Dishes, porcelain, Coors No. 4A

17. Supply of 5 and 10 ml graduated cylinders

18. Syringe, 2cc

19. Drying Oven - Forced draft, Fisher Isotemp

20. 50 ml transfer pipet, conforming to NBS specifications

21. Reagents - Toluene - conforming to ASTM D 841-50 for nitration grade. Isopropyl Alcohol - ACS reagent grade. Trichloroethylene - ACS reagent grade.

Procedure:

Sample Handling

1. Sample sizes should range from 40 to 50 g.

2. Prior to use, insert 3 rolled Kimwipes into each of a quantity of new thimbles. Place each thimble in a weighing bottle and dry, uncapped, for 1 hour at 120°C. Cap the weighing bottles and store in a desiccator until needed.

3. Weigh the weighing bottles plus thimbles to the nearest 0.001 g. Remove the Kimwipes and place the thimble in its support basket. Mount the thimble and basket in the neck of the kettle by spreading the basket's attaching wires. Clean the outside of the sample container and weigh to the nearest 0.01 g. Transfer the sample quantitatively to the thimble, wash with small amounts of toluene until clean and wipe dry with the Kimwipes. Place the Kimwipes in the thimble. Reweigh the empty bottle.

4. Add approximately 120 mls toluene to the kettle. Assemble apparatus as in Figure 2, ensuring all connections to be vapor tight. Do not use grease on the ground glass surfaces.

Extraction

5. Apply heat and adjust to maintain the reflux rate such that liquid does not overflow the thimble. Continue refluxing for 30 minutes after no water is visible in any part of the apparatus except the trap and the solvent dripping from the thimble is colorless. Discontinue heating and when refluxing has stopped, add by means of a plastic squeeze bottle, three drops of isopropyl alcohol around the inside rim of the condenser to dislodge water droplets adhering to the glass surface.

Water

6. Allow the trap and contents to cool to room temperature. Estimate the volume of water in the trap to the nearest 0.01 ml.

Solids

7. Disassemble the apparatus, remove the thimble from its support and return it to its original weighing bottle. Dry the thimbles, uncapped, for eight hours (rejects - 10 hours) at 120°C. Cool in a desiccator and reweigh.

Bitumen and Nonfilterable Solids

8. Quantitatively transfer the bitumen/solvent and nonfilterable solids fractions retained in the kettle to a 250 ml volumetric flask. Cool to room temperature and dilute to volume with toluene. Invert the flask several times to suspend the nonfilterable solids and immediately decant 75 mls to a reweighed (0.0001 g) centrifuge tube. Spin at 2000 rpm for 20 minutes. Transfer a 50 ml aliquot of the resulting bitumen/solvent solution to a porcelain evaporating dish preweighed to 0.0001 g. Discard the remaining liquid in the centrifuge tube. Wash the inner walls of the tube with toluene, being careful not to dislodge the solids present. When clean, dry the centrifuge tube plus solids at 120°C for 1 hour. Cool and reweigh.

9. Evaporate the bitumen/solvent solution contained in the evaporating dish (fume hood) until the residual solvent content approaches 1-5%. Visually, the bitumen at this point flows very slowly when the dish is tipped. Reweigh the dish plus bitumen and proceed with step 11 to determine the residual solvent content.

10. Preparation of Calibration Curve

    a) Prepare stock solutions of 20.00 g benzene-extracted bitumen per 100 ml trichloroethylene and 1.00 g toluene per 5.0 ml trichloroethylene.

    b) Prepare a series of standard solutions by combining the required volumes of toluene stock solution with sufficient bitumen stock solution in 10 ml volumetric flasks, as outlined in the following table.

% Toluene	Volume of Toluene Stock Solution (ml)
0.5	0.05
1.0	0.10
2.0	0.20
3.0	0.30
4.0	0.40
5.0	0.50
7.0	0.70
10.0	1.00

    c) Ready the IR spectrophotometer. Introduce some trichloroethylene to the reference cell and place in the reference beam. Fill the sample cell with each calibration standard and record the scans from 13 to 15 microns (665-770 cm^{-1}). Flush cells with trichloroethylene and air dry between each scan. Determine the net absorbance of each standard using the following baseline technique:

Construct a baseline by drawing a straight line tangent to the shoulders of the absorption peak at approximately 14.3 microns (699 cm^{-1}). See Figure 3. Calculate the net absorbance of this peak by subtracting the baseline absorbance from the gross absorbance of each standard.

d) Prepare the calibration curve by plotting the net absorbance of each standard versus wt % toluene on rectangluar coordinate paper. Draw the best fit through the points.

11. Residual Toluene Determination

a) Calculate the amount of trichloroethylene required to form a final volume numerically equivalent to 5 times the weight of bitumen retained in the evaporating dish.

b) Add approximately half this volume to the sample to dissolve the bitumen and quantitatively transfer the solution to a 5 or 10 ml graduated cylinder. Clean the dish with small washes of trichloroethylene, adding the rinses to the cylinder. Dilute to volume and charge a portion to the IR cell.

c) Scan the sample from 13 to 15 microns (665 to 770 cm^{-1}) and determine the net absorbance of the peak at 14.3 microns (669 cm^{-1}).

d) Obtain the weight % residual toluene in the sample from the calibration curve.

<u>Calculations:</u>

1. Tar Sand

$$\text{Water Content wt\%} = \left(\frac{V}{W}\right)(100)$$

$$\text{Solids Content wt\%} = \left(\frac{S + 3.33A}{W}\right)(100)$$

$$\text{Bitumen Content wt\%} = \left(\frac{B}{W}\right)(100)$$

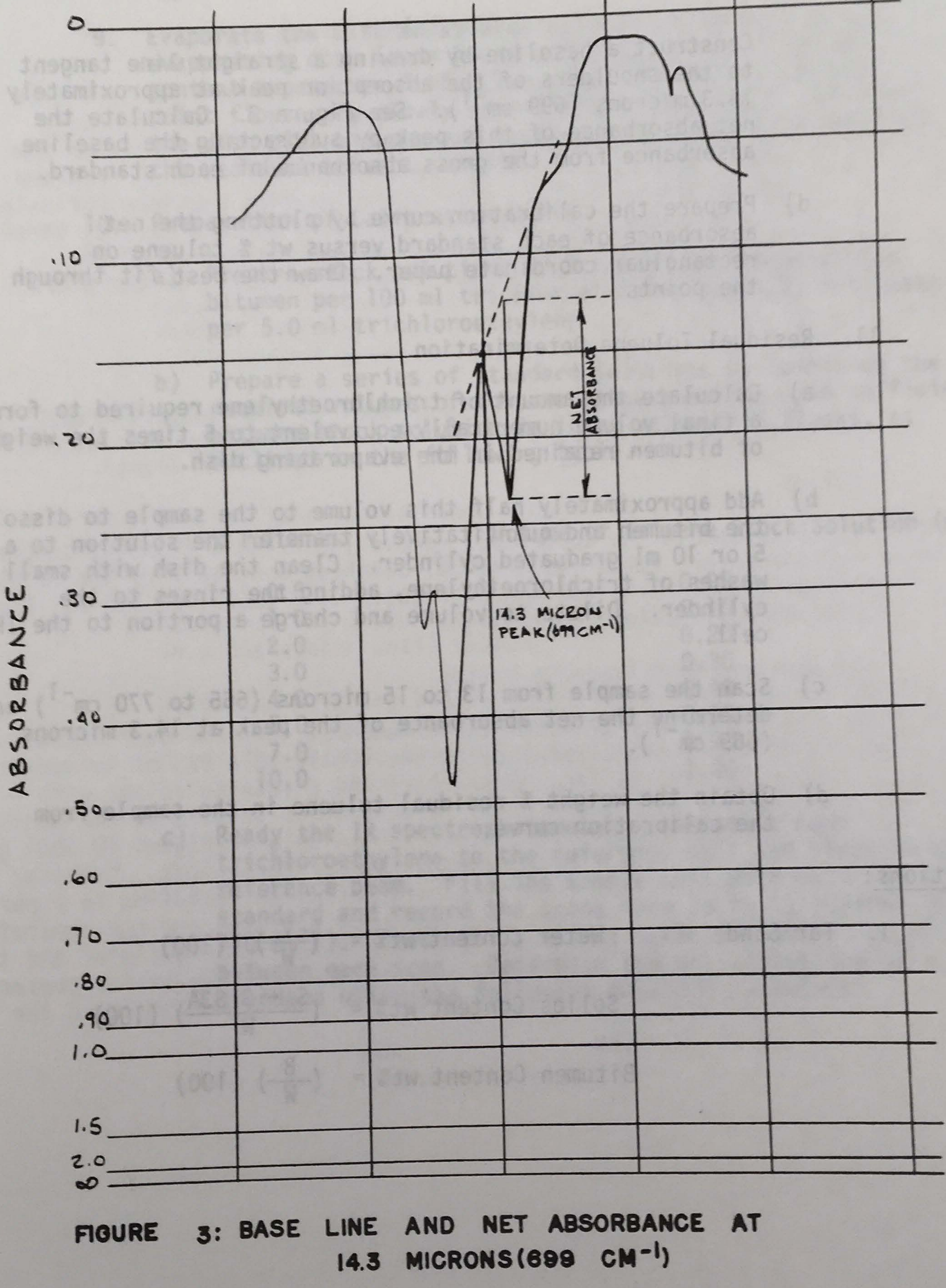


FIGURE 3: BASE LINE AND NET ABSORBANCE AT 14.3 MICRONS (699 CM^{-1})

2. Reject

$$\text{Water Content wt\%} = \left(\frac{V}{W}\right)(100)\left(\frac{100-L}{100}\right) + L$$

$$\text{Solids Content wt\%} = \left(\frac{S + 3.33A}{W}\right)(100)\left(\frac{100-L}{100}\right)$$

$$\text{Bitumen Content wt\%} = \left(\frac{B}{W}\right)(100)\left(\frac{100-L}{100}\right)$$

Where: V = ml water in trap
W = sample weight, g
S = weight of solids recovered in thimble, g
A = weight of nonfilterable solids in centrifuge tube, g
B = total bitumen weight, g = 5b (100 - T)
b = weight of bitumen in evaporating dish, g
T = weight % residual toluene
L = weight % H_2O loss, as calculated per S.A.M. 1.002

<u>Precision</u>: The repeatability of a tar sand analysis, assuming strict adherence to the procedure outlined, at the 95% confidence limits, is given below. Limits for the repeatability of a reject analysis have not been determined.

	Standard Deviation	Coefficient of Variation	Repeatability
Lean Tar Sand			
Bitumen Content, Avg. = 10.09 Wt%	0.17 Wt%	1.68 %	±0.33 Wt%
Water Content, Avg. = 3.70 Wt%	0.24 Wt%	6.49 %	±0.47 Wt%
Medium Tar Sand			
Bitumen Content, Avg. = 11.65 Wt%	0.14 Wt%	1.20 %	±0.27 Wt%
Water Content, Avg. = 2.17 Wt%	0.87 Wt%	40.09 %	±1.71 Wt%
Rich Tar Sand			
Bitumen Content, Avg. = 14.44 Wt%	0.12 Wt%	0.83 %	±0.24 Wt%
Water Content, Avg. = 0.36 Wt%	0.21 Wt%	58.33 %	±0.41 Wt%

The data shown incorporates errors due to sampling. Data from which the above values have been computed is presented in the CPA Tar Sands Council report on the "Round Robin Study of Analytical Procedures for Various Laboratories on Assay Analysis of Athabasca Tar Sands". Refer to Appendix I of this manual for definitions and information related to the derivation and interpretation of these precision values.

Comments: Elapsed time per determination - Tar Sand 12 hours
Reject 20 hours

References:

1. ASTM E123, "Apparatus for Determination of Water by Distillation"

2. C.P.A. Tar Sand Council Study, March, 1974

Origin - S.A.M. 2.1.1D, revised June, 1970 to S.A.M. 5.02A

Revised - May, 1974

Reviewed By - R.E. Hoyle, R.C. Shaw, C.G. Paton

RESIDUAL TOLUENE ANALYSIS S.A.M. 1.006

DATE ____________ TECHNICIAN ____________

CELLS ____________ CALIBRATION CURVE ____________

SAMPLE NO.	CRUCIBLE NO.	SAMPLE WT.	5 (WT.)	ABS	% RESIDUAL TOLUENE

BITUMEN, WATER, AND SOLIDS DETERMINATION-TAR SAND & REJECT

TEST DESCRIPTION ______________________ DATE __________ S.A.M. 1.006

JOAN 1

	CODE	DAY	MON.	HOUR	STR'M NO.	SAMPLE BOTTLE	BOTTLE	WATER	CENTRIFUGE TUBE	CENTRIFUGE TUBE + FINES	THIMBLE	THIMBLE +SOLIDS
101												
102												
103												
104												
105												
106												
107												
108												
109												
110												
111												
112												

JOAN 2

	CRUCIBLE	CRUCIBLE + BITUMEN	% R.T.	% LOSS
101				
102				
103				
104				
105				
106				
107				
108				
109				
110				
111				
112				

REMARKS ______________________

TECHNICIAN ______________________

APPENDIX B

Abstract, Summary, Conclusions and Recommendations from the C.P.A. Tar Sand Council Round Robin Study 1973/1974

ABSTRACT

A comparison was made of commercial and company in-house laboratory techniques used in the analysis of tar sands to determine consistency of tar assay results. Inconsistent results necessarily have an influence on tar grade and therefore ultimately on reserves (royalties) and economics of a project. The comparison was conducted through a Round Robin test procedure whereby laboratories analysed tar sand samples from a common uniformly homogenized batch. Three batches of differing tar grades were prepared and the mean, standard deviation and 95% confidence levels derived from the results were compared. The results indicated that all laboratories examined provided data within the acceptable error of accuracy expected. While good agreement existed between laboratories in general, some laboratories had much wider standard deviations than others. This test should be considered a quality controlled one and does not necessarily reflect the work expected from a laboratory conducted under "routine" conditions. Errors resulting from loss or gain of water incurred during the coring and sampling processes and their effect on "in-situ" percent bulk weight tar were analysed and found to be significant especially in the lower grade materials.

SUMMARY

A Round Robin study of assay results on various laboratories involved in analyzing tar sands was conducted by the Tar Sands Council. Such a study is an ideal method of checking consistency of results of assay techniques and laboratory methods providing that samples are uniform. With the exception of one set of samples, which was eliminated in some of the comparisons, this was achieved and the study was considered a success.

The examination of results from four in-house and four commercial laboratories indicated general good agreement amongst all laboratories with errors close to or well below the expected tolerance level. The data from two laboratories had means which compared favourably with the other laboratories but generally had wider variation. No one technique or laboratory showed superiority over another; however, the modifed Dean-Stark has the advantage of a built-in material balance check on all results.

Analysis of errors resulting from water loss or gain incurred during the coring and sampling processes indicated that the magnitude of effect on "in-situ" bulk weight tar in the range of grades examined is significant especially in the lower grades. Use of percent dry (or sand) weight is one method of eliminating the water loss or gain problem.

Continuing investigation including the fines problem and degree of accuracy expected should be made into the low tar content (6-8%) range.

CONCLUSIONS

(1) The Round Robin study indicated that all laboratories examined showed good agreement in analysis results with consistent low standard deviations. The average 95 percent confidence level values for the percent bulk weight tar and percent dry weight tar categories were very close to or below the expected tolerance of 5%. A trend of higher standard deviation and 95 percent confidence level values with lower tar content was evident.

(2) Consistency of results indicate that no one laboratory or technique showed superiority over another within the accuracy demanded for the tar grades examined. Therefore, under "controlled" conditions the data of the Syncrude laboratory employing the Modified Dean-Stark, while exhibiting very good overall consistency, was not markedly better than that obtained by the laboratories employing the conventional Dean Stark. The Modified Dean-Stark technique however has the distinct advantage of a built-in material balance check on the results. The level of consistency between the in-house and commercial laboratories was generally the same. Hydrocarb and Shell laboratory data compared favourably with other laboratories with respect to the mean but exhibited wider variation between samples and hence wider 95% confidence levels than the overall category for the bulk weight and tar weight categories.

(3) Although the ±5% acceptability tolerance was a goal set out in our terms of reference, it was obvious that a reproducibility expectation as low as ±3% with a 95 confidence level can be achieved for rich material.

(4) There was a lack of low tar saturation material in the range of 6% level in the study set and therefore reproducibility results in this range could not be examined. However, extrapolation was made and a value for 6% bulk weight tar grade, the cut-off generally used for mining exploitability, was calculated to be ±10-12% approximately.

(5) The water loss or gain errors incurred during the sampling process can be significant ones if extreme care is not taken. This is especially so in the lower tar saturation ranges where water content is higher. The problem can be avoided if the dry weight approach is used.

(6) Water losses or gains during the laboratory analytical procedure, while not quite as large in magnitude as experienced during sampling, can be as significant since they have direct effect on tar content. The problem cannot be avoided through the dry weight approach.

(7) The data obtained in the Shell A and J and Imperial sample suites indicated that even with lengthy delay, results can be achieved within acceptable limits but wider standard deviations will result due to aging, loss of water etc. This applies to tar grades examined in this report i.e. 9%-14.5% bulk weight and may not apply to more lean material.

(8) No evidence was apparent that fines escaping into the solvent phase during refluxing was a problem in the range of tar grades examined. This of course does not preclude the problem in the low bitumen-high fines material. This type of material was not available for our study.

(9) The use of assay porosity is a good qualitative guide to validity of results.

(10) This study must be considered a quality controlled one and therefore the study on the basis of routine work is lost. Quality control on routine work must be considered the responsibility of each company having work done.

RECOMMENDATIONS

(1) The anaytical data presented by commercial laboratories should include the following:

- i Percent Bulk Weight Tar
- ii Percent Bulk Weight Water
- iii Percent Bulk Weight Sand
- iv Percent Dry (Sand) Weight Tar
- v Assay Porosity as Percent Bulk Volume

The percent dry weight tar may be used for calculation of "in-situ" bulk weight tar using correct porosities. This value may be used for reserves calculations or as a check on the reported bulk weight tar data.

(2) Further investigations should be made into low bitumen content analysis problems. This should include the fines problem, and confirmation on what degree of accuracy should be expected in this regard.

(3) An investigation should be made into sampling procedures right from bit stage to extraction cup to include coring techniques, storing material in the field, transportation of material to the laboratory, sampling in the laboratory.

(4) A definite need exists for continuing research into bitumen analysis.

APPENDIX C

A Tar Sand Extraction Method for O/W/S Analysis
Proposed by D. L. Ball

Aspects of Extraction Method Development

1. Quantitatively examine various solvents and their solvent ability with respect to bitumen and water (especially extreme conditions).
   - Karl Fischer determinations on solutions containing known amounts of bitumen and water.
   - Visual and gravimetric examinations of precipitates and residues.

2. Using the proposed apparatus examine visually and gravimetrically the extraction efficiency of known amounts of bitumen and water.
   - Karl Fischer determinations to assess precision and accuracy of water results.
   - Assess precision and accuracy of evaporation method of bitumen determination using the chosen solvent system.

3. Extract previously analyzed samples of tar sand, especially extreme cases, and compare results with current method.
   - Establish optimum solvent and N_2 flows, drying times, etc., as well as sonification effect.
   - Using optimum conditions evaluate bitumen by difference possibilities.
   - Conduct a thorough precision and accuracy study of the technique versus Dean-Stark method.

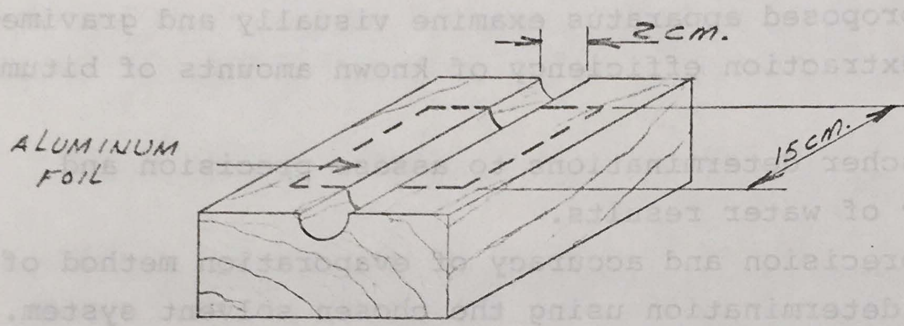
4. Explore the possibility of simultaneous water and bitumen determinations using Liquid Chromatography and the new Tracor flame ionization detector (to be marketed March, 1975), and also using N.M.R. by submitting extract samples to suppliers.

5. Examine the automation potential of the technique.
   - i.e., Karl Fischer method for water, time controlled solvent/ N_2 valve etc.

Proposed Procedure

1. Weigh a single piece of Al foil (approximately 10 x 15 cm), one Kimwipe, two glass wool plugs and the glass sample tube as a group.
   = Weight #1

2. Place the Al foil into the wooden mould and form into the slot as shown:



3. Quickly place the frozen sample in the slot, wipe the sample container with the weighed kimwipe, fold and place the latter at one end of the slot.

4. Bring the edges of the foil together, pinch at the base, lift from the mould and quickly fold the edges over to form an open ended tube.

5. Insert the foil wrapped sample into the glass sample tube according to the diagram, insert the glass wool plugs and weigh the entire assembly.
   = Weight #2

6. Connect the one holed stoppers to the sample tube and lower into the sonification bath at approximately a 45^{o} angle.

7. Start the sonification bath as well as the solvent flow and set the flow to 15 ml/min (estimated) and for a total period of 15 minutes (estimated).

8. Then switch from solvent to N_2 drying for a total period of 10 minutes (estimated).

9. After solvent has ceased flowing remove the volumetric flask, bulk to the flask volume, shake thoroughly and remove aliquots for Karl Fischer water, and when required, for bitumen determinations.

10. At the end of 10 minutes N_2 flow wipe the exterior, remove the stoppers and allow the sample tube to cool and air dry for another 10 minutes.

11. Weigh the sample tube.
= Weight #3

12. Remove the glass wool plugs and discard the plugs and the foil wrapped sample leaving the sample tube ready for the next analysis.

Calculations

Total Sample or Bulk Weight = Weight #2 - Weight #1
Solids Weight = Weight #3 - Weight #1

$$\% \text{ Solids} = \frac{\text{Solids Weight}}{\text{Bulk Weight}} \times 100\%$$

Water Weight = a) Karl Fischer result x $\dfrac{\text{Volumetric Flask Volume}}{\text{Aliquot Volume}}$
or
b) By Liquid Chromatography, M.M.R. etc.

$$\% \text{ Water} = \frac{\text{Water Weight}}{\text{Bulk Weight}} \times 100\%$$

Bitumen Weight =

Options

a) By difference:

= Bulk weight - (Solids + Water Weight)

or

b) By evaporation:

= Aliquot Residue Weight x $\dfrac{\text{Volumetric Flask Volume}}{\text{Aliquot Volume}}$

- Residual Solvent Correction

or

c) By Liquid Chromatography, etc.

$$\% \text{ Bitumen} = \frac{\text{Bitumen Weight}}{\text{Bulk Weight}} \times 100\%$$

A Tar Sand Extraction Method for O/W/S Analysis Proposed by D.L. Ball